

Copolymerization of Ethylene and Unsaturated Fatty Acid and Gum Naval Stores Compounds

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The report summarizes a research project to explore the copolymerization, by the continuous, high pressure, free-radical process, of ethylene and various chemicals derived from fatty acid or gum naval stores compounds. The objective of the investigation was to develop a new, potentially large outlet in the plastics industry for certain sure polymerizations of ethylene agricultural chemicals. While the literature includes a few references to such copolymers¹⁻⁷ and each industrial research organization active in high pressure polymerizations of ethylene has undoubtedly studied a few others, it is believed that such copolymerizations have not been

SUMMARY

Sixteen comonomers were selected for evaluation in this programme. These compounds represented materials with from one to three double bonds per molecule, conjugated and non-conjugated structures, and different chemical classifications (aliphatic, aromatic, acid, ester, and amide).

Most of the comonomers were commercial grades and contained varying quantities of the naturally occurring isomers.

Each of the comonomers was copolymerized with ethylene at three different sets of reaction conditions to characterize the materials on a broad scale. Additional copolymers were then synthesized to further evaluate those comonomers that appeared capable of yielding resins with commercial potential.

studied before in a comprehensive test programme.

EXPERIMENTAL

Table 1 shows the unsaturated fatty acid and gum naval stores compounds which were used as comonomers in this study. All of the comonomers, except erucylamide, were pumped into the ethylene stream ahead of the

feed compressor. They were used either as-received or diluted with an inert solvent such as benzene. Erucylamide, however, was dissolved in hot toluene and pumped directly to the reactor through a separate, heated line. This was necessary since the comonomer would precipitate and plug the lines if it were mixed with the ethylene ahead of the reactor.

The copolymerizations were carried out in an autoclave-type reactor by the continuous, high pressure process.⁸ Fig. 1 is a flow diagram of the synthesis system. Reaction was initiated and sustained by free-radical producing initiators of the peroxide type. Initiators or catalysts were selected on the basis of free radical activity at the desired reaction temperature.

Three synthesis runs were attempted with all of the comonomers listed in Table 1 except "Staybelite" resin. The reaction conditions were:

1. 20,000 psi, 440°F., with 3% comonomer in the feed.
2. 12,000 psi, 330°F., with 10% comonomer in the feed.
3. 12,000 psi, 330°F., with the maximum possible comonomer content in the feed.

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Table II

ASTM PROCEDURES FOR PHYSICAL PROPERTIES	
Resin Property	ASTM Procedure
Melt Index, g/10 min.	D 1238-65T
Density, g/cm ³	D 1505-63T
Haze, %	D 1003-61
Gloss, %	D 2457-65T
Elmendorf Tear, psi	D 1922-61T
Friction Factor	D 1894-63
Dart Drop, mil/gm	D 1709-62T
Elongation, %	D 638-64T
Tensile Strength, psi	D 638-64T
Yield Strength, psi	D 638-64T
Modulus, psi	D 638-64T
Torsional Stiffness, psi	D 1043-61T
Low Temperature Brittleness, °C., F/50	D 746-64T
Stress Crack, hr, F/50	D 1693-60T
Vicat Softening Point, °C.	D 1525-58T

through the reactor jacket, and injecting catalyst solution into the reactor to initiate polymerization.

After a few minutes, in which conditions were stabilized, the experimental comonomer was introduced into the ethylene stream at a low rate. The comonomer and ethylene rates were gradually adjusted to the specified values, and the catalyst rate was regulated to maintain the desired reaction temperature.

Where possible, the copolymers were subjected to a series of physical tests to determine processing characteristics, resistance to environmental exposure, mechanical properties, and product composition. The properties tested and the ASTM procedures used are listed in Table II. Several of the products had melt flow rates that were above the range of D-1238-65T. In those cases, melt flow rates were determined using non-standard melt indexer conditions. Such melt flow rates were converted, using factors developed for polyethylene, to values called "equivalent melt indexes". Also determined for all products were polymer content (by removal of unreacted comonomer), and comonomer incorporation in the solid product (by infrared spectroscopic techniques).

COMONOMER CHARACTERIZATION

The comonomers listed in Table 1, except "Stay-

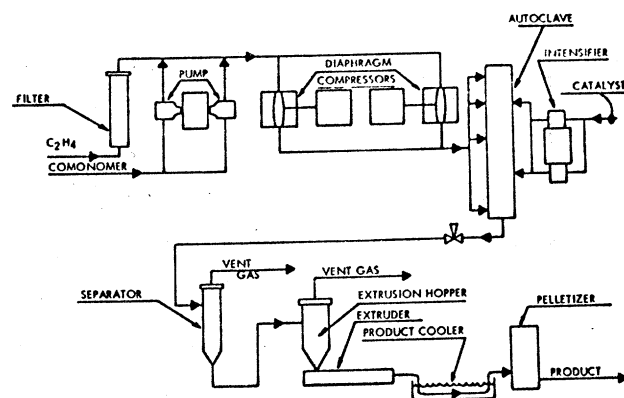


Fig. 1: A flow diagram of the synthesis system.

belite" resin, were mixed with ethylene and subjected to three different combinations of concentrations and reactor conditions. In this part of the programme, there were no product specifications (such as specific melt index range).

Everything that came out the extruder die was considered as in-grade product, provided the

Table III

MONOMER REACTIVITY	
Monomer	Monomer Reactivity (Wt., % Monomer in Polymer) (Wt., % Monomer in Feed)
Alpha Pinene	0.4
Erucylamide	0.77
Methyl Esters of Castor Oil Acids	0.77
Methyl Oleate	0.56
Methyl Undecenoate	1.2
Vinyl Laurate	1.3
3,7-Dimethyl-1, 6-Octadiene	0.18
Dipentene—High Purity	0.57
Methyl Esters of Safflower Oil Acids	0.70
Gum Rosin	1.8
Methyl Esters of Conjugated Safflower Oil Acids	1.2
Methyl Esters of Dehydrated Castor Oil Acids	2.5
Methyl Esters of Linseed Oil Acids (at 330°F.)	0.87
Methyl Esters of Linseed Oil Acids (at 440°F.)	4.1
Alloocimene	2.0
Methyl Esters of Tung Oil Acids	3.9
Myrcene	1.3

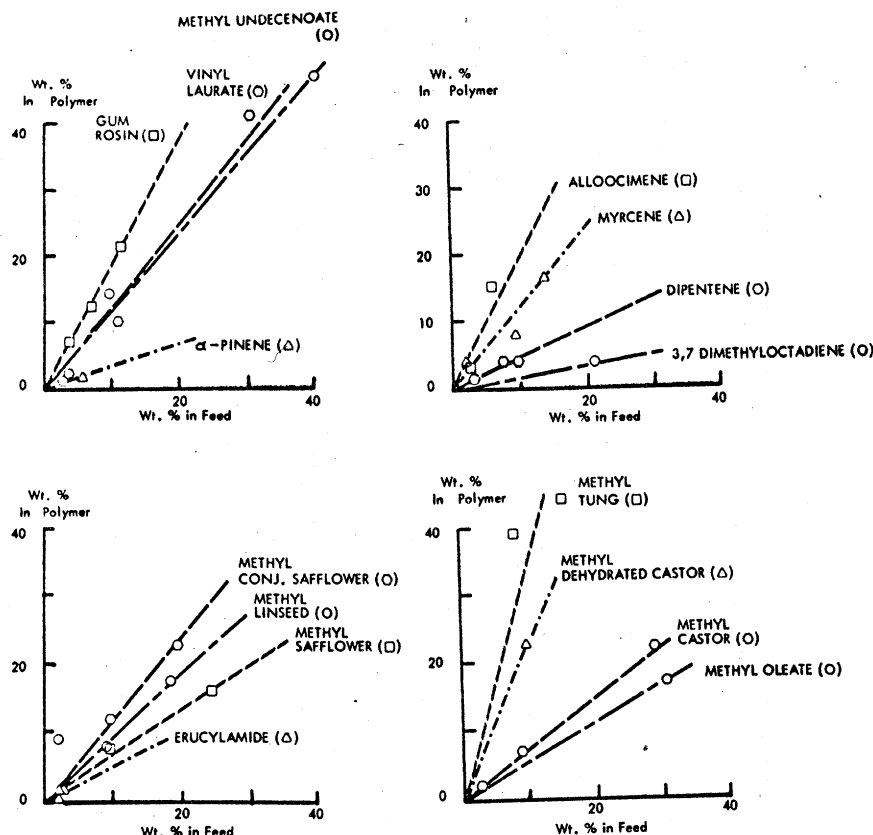


Figure 2.

flow rates and reactor conditions were reasonably close to the desired values. Only two of the comonomer characterization

runs had to be abandoned because of operating difficulties. Methyl esters of tung oil acids and alloocimene both led to un-

stable reactions at condition "1" (440°F., 20,000 psi, 3% comonomer in feed), and efforts to bring the reactions under control were unsuccessful.

A number of other runs also presented operating problems, but were eventually completed successfully, though it was sometimes necessary to compromise a few run specifications in order to consider certain of these runs successful. Some of the more difficult runs were those at conditions "2" and "3" (10% and maximum, respectively, comonomer in the feed, both at 330°F. and 12,000 psi) with methyl esters of tung oil acids and alloocimene and condition "1" with myrcene. It should be noted that methyl esters of tung oil acids and alloocimene both have three conjugated double bonds per molecule. Myrcene also has three double bonds per molecule, two conjugated and one that is isolated.

The products all had low molecular weights. Several of them had liquid phases. Analysis of the liquids showed them to be high in comonomer content.

For most of the comonomers, the incorporation in the solid portion of the product was dependent only on the comonomer concentration in the feed and not on reaction temperature or pressure. This is shown in Fig. 2, where the concentrations and incorporations are expressed as weight percentages. Methyl esters of linseed oil acids, however, had a higher incorporation in the polymer made at 440°F. and 20,000 psi than would be indicated by the line drawn in Fig. 2, in which the data at 330°F. and 20,000 psi were used to re-

Table IV

EFFECT OF MONOMER TYPE ON CATALYST EFFICIENCY

Number of Double Bonds per Molecule	Catalyst Efficiency, lb product/lb catalyst	
	Not Conjugated	Conjugated
1	316, 208, 540 280, 840, 1, 850	Not possible
2	910, 39,* 334	77, 25, 35
3	122	9

*High purity dipentene

Operating Condition "1": 440°F., 20,000 psi, 3% comonomer.

For normal operation under these conditions, catalyst efficiency would be about 1,800 lb polymer/lb catalyst.

present this comonomer. Later work at 440°F. with methyl esters of linseed oil acids at lower feed concentrations correspond closely with the value obtained at 330°F.

The slopes of the lines in Fig. 2 were used to characterize the comonomer reactivities. These values are presented in Table III. Of the comonomers with one double bond per molecule, it was observed that monomer reactivities on a weight basis were higher when the double bond was in the terminal position. Comonomers with two or three conjugated double bonds had higher comonomer reactivities than their nonconjugated counterparts.

One of the most noticeable results of adding these comonomers to the polymerization was a reduction in catalyst activity. The catalyst efficiencies roughly correlated with the type and amount of unsaturation as shown in Tables IV and V. In these tables, note that the efficiencies were based on the total product collected.

Many of the efficiencies would be much lower if they were based only on the solid polymer produced. Except for alpha pinene and methyl oleate, the comonomers with one double bond per molecule were involved in at least one run in which the catalyst efficiency was normal. In general, catalyst efficiencies decreased as the comonomers increased in unsaturation. Conjugated double bonds in a comonomer also tended to result in a lower catalyst efficiency.

The values that represent catalyst efficiencies in the high purity (>95%) dipentene polymerizations are identified in Tables

Table V

EFFECT OF MONOMER TYPE ON CATALYST EFFICIENCY		
Condition "2", Monomer Concentration — 10%		
Number of Double Bonds per Molecule	Catalyst Efficiency, lb product/lb catalyst	
	Not Conjugated	Conjugated
1	63, 94, 57, 50, 440, 14	Not possible
2	6,* 17, 30	18, 9
3	19	12, 4, 6
Condition "3", Monomer Concentration — Maximum		
Number of Double Bonds per Molecule	Catalyst Efficiency, lb product/lb catalyst	
	Not Conjugated	Conjugated
1	456, 63, 7, 41, 26, 132	Not possible
2	26, 5,* 11	18, 18, 12
3	13	14, 4, 5
*High purity dipentene		
Operating Conditions: 330°F., 12,000 psi		
For normal operation under these conditions, catalyst efficiency would be about 110 lb polymer/lb catalyst.		

IV and V. These values were unusually low compared to those for other comonomers in the same classification. Commercial-grade dipentene (about 70% pure) was originally used in runs at conditions "1", "2", and "3", and the values obtained were even more out of place.

PRODUCTION AND EVALUATION OF SELECTED COPOLYMERS

This phase of the project was to prepare and evaluate additional ethylene copolymers using

those comonomers that showed the highest potential of yielding useful products. Certain copolymers were synthesized to provide material for additional tests, and some copolymerizations were to verify or extend information gained in the characterization part of the project. One new hydrogenated wood resin comonomer, the "Staybelite" in Table I, was included in a comparison with gum resin.

Table VI is a summary of the synthesis conditions and melt indices of the copolymers selected

Table VI

SUMMARY OF THE SECOND SERIES OF COPOLYMERIZATIONS

Comonomer	% Comonomer		Reaction Conditions	
	in Feed	Melt Index	psi	°F.
Alpha Pinene	0.5	3	22,000	440
Erucylamide	(2)	3	22,000	440
Erucylamide	(2)	3	20,000	440
Methyl Esters of Castor Oil Acids	0.6	3	22,000	440
Methyl Esters of Castor Oil Acids	0.1	3	22,000	440
Methyl Esters of Castor Oil Acids	0.3	3	22,000	440
Methyl Esters of Castor Oil Acids	1.3	20	22,000	300
Methyl Esters of Castor Oil Acids	0.7	0.5	22,000	300
Methyl Oleate	0.3	3	22,000	440
Methyl Oleate	1.1	3	22,000	330
Methyl Oleate	2.1	20	22,000	300
Methyl Undecenoate	0.2	9	22,000	440
Methyl Undecenoate	1.0	3	22,000	330
Methyl Undecenoate	1.3	28	22,000	300
Methyl Undecenoate	19	>110,000	22,000	300
Vinyl Laurate	2.9	3	22,000	440
Vinyl Laurate	2.3	3	22,000	330
Vinyl Laurate	4.5	14	22,000	300
Vinyl Laurate	17	25,000	22,000	300
3,7-Dimethyl-1,6-Octadiene	0.3	5	22,000	440
Dipentene	0.1	23	22,000	300
Methyl Esters of Safflower Oil Acids	0.4	3	22,000	440
Methyl Esters of Safflower Oil Acids	0.1	3	22,000	440
Methyl Esters of Safflower Oil Acids			Cyclohexane ⁽³⁾	
Gum Rosin	10	65,000	20,000	330
"Staybelite" ⁽¹⁾ Rosin	9	50,000	20,000	330
Methyl Esters of Dehydrated Castor Oil Acids	3.4	22	22,000	440
Methyl Esters of Dehydrated Castor Oil Acids	0.1	21	22,000	440
Methyl Esters of Dehydrated Castor Oil Acids			Cyclohexane ⁽³⁾	
Methyl Esters of Dehydrated Castor Oil Acids	0.2	3	22,000	440
Methyl Esters of Linseed Oil Acids	0.3	21	22,000	440
Methyl Esters of Linseed Oil Acids	0.1	23	22,000	440
Methyl Esters of Linseed Oil Acids			Cyclohexane ⁽³⁾	

(1) Hercules Powder Company brand of hydrogenated wood rosin.

(2) Abandoned.

(3) Required for melt index control.

for further evaluation. No additional copolymers were produced with methyl esters of conjugated safflower oil acids, allocimene, methyl esters of tung oil acids, or myrcene.

Two synthesis runs that involved erucylamide could not be made. Both were intended to produce film grade resin while using the erucylamide feed rate to control the product melt index. In both cases, difficulty was encountered in pumping the monomer solution to reaction pressure. Reaction pressure in the first run was 22,000 psi and in the second it was 20,000 psi.

Alpha pinene, 3,7-dimethyl 1-1,6-octadiene, and the methyl esters of safflower oil acids did not significantly influence the polymer properties when added separately to the ethylene polymerization in the small quantities needed for melt index control. In other words, the product was typical of polyethylene that would have been made at the same synthesis conditions with a low molecular weight hydrocarbon for a modifier (cyclohexane, for instance) rather than the experimental comonomer. Of the three, dimethyl octadiene was the most efficient modifier from the standpoint of the amount required at a given set of polymerization conditions to yield a product with a given melt index. It was also noted that the presence of 0.4% methyl esters of safflower oil acids in the reactor caused a drastic reduction in the catalyst efficiency.

Several copolymerizations were made with the methyl esters of castor oil acids. It was found that, when the reaction was car-

ried out at 22,000 psi and 450°F., 0.1% of this comonomer in the reactor feed resulted in a resin that produced blown film with a slightly lower friction factor (0.3 versus 0.7) than a comparable polyethylene. With 0.3% or more of this comonomer in the feed at the reaction conditions described above, copolymers were produced that exuded an oily material over a period of time. The two methyl castor oil copolymers synthesized at 22,000 psi and 300°F. were oily also, and contained only about 80% solid polymer.

Polymer produced with 0.3% methyl oleate in the reactor and conditions of 22,000 psi and 440°F., had good resistance to stress cracking. Two other runs were made to investigate the stress crack resistance of copolymers with higher melt indices and high methyl oleate incorporations. Neither of the resins produced in these runs exhibited an unusual degree of stress* crack resistance.

Four synthesis runs were made with methyl undecenoate. The first was made at a pressure of 22,000 psi and a temperature of 440°F., and required only 0.2% methyl undecenoate in the feed to produce a material with a melt index of 9. A great deal of difficulty was encountered at these conditions because the reaction tended to die. Properties of the resin, which had a methyl undecenote incorporation of 0.1%, were not significantly different than those of a comparable polyethylene.

In another polymerization, carried out at 22,000 psi and 300°F., 1.3% methyl undecenoate in the reactor yielded a 28 melt index

Table VII

INFLUENCE OF ROLL MILLING ON MELT INDEX OF ETHYLENE-DRYING OIL COPOLYMERS					
Run Number	297	298	293	294	Poly- ethylene
Comonomer	Methyl De- hydrated Castor Oil	Methyl De- hydrated Castor Oil	Methyl Linseed Oil	Methyl Linseed Oil	None
Incorporation	0.71	0.15	0.42	0.09	None
Melt Index in August, 1965	22.0	21.3	20.7	22.7	Not run
Melt Index in April, 1966—					
Start	20.8	20.9	19.1	22.1	22.2
Roll Milled 10 min.	19.1	19.0	17.4	20.2	21.6
Roll Milled 20 min.	18.7	18.0	16.6	20.4	21.2
Roll Milled 30 min.	18.1	18.0	16.6	19.8	22.1
Roll Milled 40 min.	17.4	17.2	16.7	20.0	21.7
Roll Milled 50 min.	17.4	17.8	16.2	20.1	21.2
Roll Milled 60 min.	17.4	17.7	15.6	19.2	21.7
Melt Index Decrease, %	16.3	15.3	18.3	13.1	2.25

resin which had lower tensile strength, modulus of elasticity and brittleness temperature than a comparable polyethylene.

With 19% methyl undecenoate in the reactor feed and reaction conditions of 22,000 psi and 300°F., the product had an equivalent melt index of over 100,000 and contained only 34% solid polymer. The polymer portion of the product had a methyl undecenoate incorporation of 20%.

Catalyst efficiencies for the last three syntheses mentioned were only 10 to 20% of the values that would have been obtained in a normal ethylene polymerization at similar reaction conditions.

Vinyl laurate was copolymerized with ethylene under four sets of conditions. A 3 melt index resin was produced at 22,000 psi and 440°F. with 2.9% vinyl

laurate in the feed. With 2.3% vinyl laurate in the reaction at 22,000 psi and 330°F., the product had a melt index of 3. Each of these resins had a vinyl laurate incorporation of about 1%, and, compared to corresponding polyethylene, had lower tensile strength, modulus of elasticity, torsional stiffness, and Vicat softening point, and higher stress crack resistance. In addition, the product made at 330°F. had a low density and contained only 88% solid polymer.

Ethylene-vinyl laurate copolymer synthesized at 22,000 psi and 300°F. with 4.5% vinyl laurate in the reactor feed, had a melt index of 14. Its physical properties were similar to comparable polyethylene except that the density was lower and it was much more resistant to stress cracking. Also, the polymer con-

Table VIII

EXPERIMENTAL COPOLYMERS AS SLIP AGENTS IN FILM

Slip Agent Comonomer	None None	Amide E* None	#225-4 Erucyl- amide	#53 Methyl Oleate
Comonomer Concentration in Product, %	—	—	27	11.7
Base Resin	NA 280	NA 280	NA 280	NA 280
Intended Comonomer Concentration, ppm	None	1,000	1,000	1,000**
Amide, ppm	—	950	1,520	<50
Ash, ppm	—	20	0	—
Film Haze, %	—	5.2	5.1	4.8
Film Gloss, %	—	10.3	10.5	10.5
Friction Factor	0.51	<0.07	0.07	0.7

* Humko Products Company brand of erucylamide.

** Methyl oleate content of film 0.11% (1,100 ppm) by IR.

tent in the product was only 79%.

While these vinyl laurate copolymers all had a desirable feature in the good stress crack resistance, they also had a drawback in the form of an irritating, disagreeable odour.

With 17% vinyl laurate in the feed to the reactor, and reaction conditions of 22,000 and 300°F., material with an equivalent melt index of 25,000 was produced. This material contained 48% solid copolymer which had a vinyl laurate incorporation of 8%.

One synthesis run was made to evaluate dipentene as a modifier in the ethylene polymerization. At reaction conditions of 22,000 psi and 300°F., only a 0.1% dipentene (commercial grade) was required to produce a 23 melt index resin. Compared to polyethylene of the same melt index which was synthesized at the same conditions, except that cyclohexane was the modifier, the resin made with dipentene had lower elongation and soften-

ing point values, lower volatiles content, and a higher brittleness temperature.

The ethylene-gum rosin copolymers of the comonomer characterization study were observed to have lost their surface tackiness and formed a brittle outer skin after a few months in a sealed container. In order to enable observation of such changes, a fresh ethylene-gum rosin copolymer was made. Another copolymer was also made with hydrogenated rosin. The hydrogenated rosin used was a partially hydrogenated grade of wood rosin commercially available from Hercules Powder Company under the trade name of "Staybelite". Duplicate runs were set up with target conditions of 20,000 psi, 330°F., and 10% rosin in the feed stream. Both runs had poor catalyst efficiencies. The product made with gum rosin had an equivalent melt index of 65,000, a polymer content of 38%, and a gum rosin incorporation in the polymer of

14%. Product from the hydrogenated rosin run had an equivalent melt index of 50,000, a polymer content of 46%, and a comonomer incorporation in the polymer of 5.7%. All values reported for these resins were determined about four months after the resins were produced. Equivalent melt index values determined during those first four months did not show any trends, and suggested that the resins may not have been blended sufficiently before being sampled. samples submitted over a two month period showed a decrease in equivalent melt index for both the copolymers. In this final two month period the equivalent melt index of the gum rosin material decreased by 18%, and the hydrogenated rosin material decreased by 29%.

From these observations, it is concluded that, as expected, gum rosin is more reactive toward ethylene than is hydrogenated rosin, but that the properties of the bulk material (the copolymer combined with unreacted rosin) are very similar.

Two copolymers each were made with methyl esters of dehydrated castor oil acids and methyl esters of linseed oil acids to investigate the potential of using the drying properties of these two comonomers. Of the drying oil esters in the project, these two were chosen for further work because they had the least adverse effects on the reaction and catalyst efficiency. The synthesis conditions were as follows: both runs with each comonomer were at 22,000 psi, 440°F. to produce 20 melt index resin; in one polymerization, the comonomer rate was to control

the product melt index, while in the other the comonomer rate was a fixed 0.1% of the feed rate with cyclohexane added for melt index control.

The above synthesis conditions yielded resins that had 0.71% methyl dehydrated castor oil (#297), 0.15% methyl dehydrated castor oil (#298), 0.42%, and 0.09% methyl linseed oil (#293 and #294).

After production, the methyl dehydrated castor oil copolymers, #297, and #298, and the methyl linseed oil copolymers, #293 and #294 were sealed in airtight metal containers until a test of their cross-linking tendencies could be made. This test involved working the resin for an hour on a laboratory-size, two-roll mill and taking small samples for melt index determinations at ten-minute intervals.

Also, most of the subject comonomers were oily and could be expected to act as lubricants to reduce the sliding friction between two layers of film. It was already mentioned that copolymerization runs were made to synthesize film grade resins containing small amounts of the methyl esters of safflower oil acids and methyl esters of castor oil acids as slip agents. Film friction factor of one resin made with methyl esters of castor oil acids showed a slight improvement compared to similar film made without the ester, but film prepared from the methyl esters of safflower oil copolymer showed no improvement. Another approach was to use a copolymer containing a high concentration of the experimental comonomer as the slip agent, and blend a small amount of it into a film

Table IX

**COPOLYMERS SELECTED FOR POWDER-COATING
MILD STEEL PANELS**

Resin	Comonomer	Adhesion*	Appearance
NA 202-27	None	Good	Good
#354	Methyl Castor Oil	Very poor	Good**
#357	Methyl Oleate	Fair	Good
#281	Methyl Undecenoate	Very Good	Poor
#202	Vinyl Laurate	Very Good	Good
#304	Vinyl Laurate	Poor	Poor
#359	Dipentene	Good	Good
#297	Methyl Dehydrated Castor Oil	Poor	Good
#298	Methyl Dehydrated Castor Oil	Poor	Good
#294	Methyl Linseed Oil	Poor	Good

*A narrow strip was cut in the coating and an attempt was made to remove this strip using the knife point.

**Surface was greasy on ageing.

grade copolymer. This was done with erucylamide (#225-4) and methyl oleate (#53). #225-4 was a paste composed of liquid and solid components with an overall erucylamide concentration of 27%. This figure was used to calculate the amount of copolymer to add to a film grade resin to yield 1,000 ppm erucylamide in the blend. Blending was done on a 2-lb-per-charge Banbury. The film grade resin used was Petrothene (R) NA 280 without additives. In Table VIII, the film properties of the starting resin, and resin containing a standard slip agent, Humko "Amide E", are listed for comparison with the experimental formulations. The friction factor of film that used #225-4 as the slip agent was 0.07 compared to <0.07 for "Amide E" slip agent, and 0.51 for NA 280 without additives.

Methyl oleate copolymer was also tested as a slip agent in NA 280. #53, with 11.7% methyl

oleate, was blended with base resin to give a slip level equivalent to 1,000 ppm methyl oleate. Film properties for this combination are also shown in Table VIII. Methyl oleate copolymer was not effective as a slip agent.

Another possible application for the subject copolymers is in the coating of various substrates. Ten of the copolymers were tested in the powder coating of mild steel panels. The copolymers selected for this evaluation were those with melt indices of about 20. Copolymers evaluated contained: 1.4% vinyl laurate, 2.6% vinyl laurate, 2.0% methyl undecenoate, 0.71% methyl esters of dehydrated castor oil acids, 0.42% methyl esters of linseed oil acids, 0.09% methyl esters of linseed oil acids, 0.90% methyl esters of castor oil acids, 0.84% methyl oleate, and 0.11% dipentene. The resins were prepared for coating by grinding to minus 20 mesh on a laboratory Wiley mill. Mild steel panels (3 x 6 x

0.05ins.) were prepared by cleaning with a wire brush on a grinder and degreasing with acetone. Each panel was preheated for ten minutes at 220°C. (428°F.) in a hot air oven. The panel was removed from the oven and powdered resin was sprinkled on the panel as soon as possible.

After a few seconds, the panel was turned over to allow the excess powder to drop off. The coated panel was then returned to the oven in a horizontal position with the coating on top for a post-heating period of seven-minutes at 220°C. (428°F.). The samples were removed from the oven and allowed to cool. After cooling, the coated panels were rated for adhesion and surface appearance. These ratings are listed in Table IX along with ratings for NA 202-27, a commercial Petrothene included for comparison. Vinyl laurate (#202), methyl undecenoate (#281), and

dipentene exhibited acceptable levels of adhesion to mild steel. In fact, the vinyl laurate and methyl undecenoate resin adhesion ratings were better than that of the NA 202-27. The difference in adhesion of the two vinyl laurate resins in the test is probably associated with the difference in comonomer incorporation. #202 had a dry surface and contained 98.2% solid copolymer with a vinyl laurate incorporation of 1.4%. #304, however, had an oily surface and contained only 78.7% solid copolymer which had a vinyl laurate incorporation of 2.6%.

Because of limited time, it was not possible to test the subject copolymers in all of the areas where they could prove useful. Certain of the copolymers could be of value as hot melt coatings and adhesives, either alone or in combination with various waxes and other thermoplastic

materials; or as precoats in the production of resin-coated substrates.

Some of the low molecular weight copolymers of drying oil esters could be useful in paint formulations. In the same manner, low molecular weight copolymers of other materials tested in the project could be useful as improvements in the areas where the comonomers currently have applications. Other possibilities are lubricating oil additives, paraffin modifiers, and resin plasticizers.

REFERENCES

1. Polyethylene, Interscience, New York, 1956, pp. 114-133.
2. Polyethene, Renfrew and Morgan, Interscience, New York, 2nd Ed., 1960, pp. 345-388.
3. U.S. Patent 2,611,788.
4. U.S. Patent 2,556,158.
5. U.S. Patent 2,402,137.
6. U.S. Patent 2,457,229.
7. Bates et al., J. Chem. Soc., 1962, 1521, 1531.
8. Albright, L. F., "High Pressure Processes for Polymerizing Ethylene", Chemical Engineering (Dec. 19, 1966) pp. 113-120.

GAMEWELL INTRODUCES NEW SMOKE DETECTOR

A new ionization detector, claimed to be the most sensitive unit available, has been introduced by the Gamewell Division of the E. W. Bliss Company.

One of the detector's big advantages, according to Gamewell, is its ability to sense invisible particles released in the area of an incipient fire. Prior to the start of any fire, minute, invisible particles are released from the area of a potential fire. These particles are in existence long before either smoke or heat become evident therefore the new Bliss-Gamewell detector, known as the FT-100, gives a much

quicker warning than conventional devices.

According to Gamewell, the detector's extreme sensitivity makes it ideal for use in white or "clean" rooms, computer and electronic equipment facilities. The sensitivity setting is adjustable for use in commercial buildings, warehouses, institutions, schools and manufacturing, and industrial process plants.

In triggering an alarm system, the ionization smoke detector unit may be used with annunciator circuit in the same manner as an automatic fire detector or manual non-code situation. While the FT-100 is designed primarily for overhead ceiling mounting, it

may also be used in air-conditioning return ducts

Specifications for the unit are: Voltage: 21-24 volts DC, 2 watts. Dimensions: 2½" high, 5¾" diameter. Weight: 2 lbs., shipping, 1 lb. 5 oz. nett. Integral Relays: Trouble relay, normally closed contacts (open on trouble), hermetically sealed, 0.10 ampere, 120 volts AC-DC contacts. Alarm relay, normally open (close on alarm), hermetically sealed, 0.10 ampere, 120-volts AC-DC contacts.

For further information, write Bliss International, E. W. Bliss Company, 217 Second Street, N.W., Canton, Ohio 44702, U.S.A.